



Characterization of Drawn Polyethylene by Solid State ^{13}C Magic Angle Spinning NMR

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Received May 14, 1998

Abstract: Drawn polyethylene was studied by ^{13}C cross polarization magic angle spinning techniques. Solid-solid phase transition from orthorhombic to monoclinic crystalline phase by drawing was observed. In addition, using a synchronized magic angle spinning 2 dimension technique, we confirmed that macroscopic ordering of the polyethylene was produced by drawing.

Mechanical properties of polymers are closely related with morphological properties including ordering of molecules in polymers.¹ Drawing is known to induce macroscopic molecular ordering along drawing direction.² Solid-solid phase transition from orthorhombic to monoclinic crystalline phase in polyethylene(PE) during powdering process at liquid nitrogen temperature (77K) was also reported.³ In this work, we would like to focus on the study of morphological change in PE induced by drawing. To detect phase transition, integrated areas of methylene peaks from each phase in the spectra obtained by MAS-without-CP technique were compared.³ A synchronized MAS 2 dimension (sync-MAS 2D) technique^{4,5} is employed to confirm molecular ordering along drawing direction. This NMR technique was originally developed in H. W. Spiess's group and demonstrated with drawn PE.⁵ Difference between our work and theirs with respect to applying a sync-MAS 2D technique to PE is that our sample is high density PE while theirs is highly oriented PE. Another difference is that their film samples were stacked and pressed at 300 bar into a 1.5 cm thick block while our samples were not applied any pressure after drawing. If samples have random orientation such as in powder samples or all molecules in the sample are aligned along the rotor axis, MAS NMR signal at any phase of rotor cycle would be the same.⁴ However, if samples have some degrees of order in macroscopic orientation along a direction not parallel to a rotor axis, MAS spectra strongly depend on when NMR signal

acquisition starts with respect to phases of a rotor cycle. Taking advantage of this phenomenon, we can make NMR signal acquisition be synchronized with a rotor cycle and start at specific phase of a rotor cycle for each file to measure ordering of molecules in a sample. In a sync-MAS 2D, phases of a rotor cycle at which NMR signal acquisition starts are incremented by a constant delay time value. Since each carbon site can be distinguished in ^{13}C CP-MAS spectra, ordering information of each carbon site can be obtained with a sync-MAS 2D technique by analysis of signal pattern in the 2D. Due to many spinning side bands produced from large chemical shift anisotropy (CSA), it is easier to interpret sync-MAS 2D data of carbons with a relatively large CSA. Unfortunately, PE is mainly composed of methylene carbons which is known to have a small chemical shift anisotropy.⁶ To overcome the difficulty, slow spinning rate and high magnetic field were employed.

EXPERIMENTAL

Materials

PE was taken from a commercial ondol⁷ pipe manufactured by Samsung. The PE is 2 mm thick and supposed to be cross-linked more than 75 %. Powdered PE was prepared by grinding with a freezer/mill (Spex industries Inc., U. S. A.) for 5 minutes at liquid nitrogen temperature, 77 K. Drawn PE was prepared by stretching PE of 2 mm thick until the thickness was reduced to ~ 1 mm. Drawn PE was sliced and placed in a 4 mm rotor as shown in Fig. 1. A slice of PE has a dimension of about $1 \times 1 \times 8$ in mm. Two slices of PE were enough to fill the rotor and KBr powder was used to fill the empty spaces of the sample filled rotor. It is critical to have uniform distribution of mass in a rotor in order to have stable spinning.

NMR Spectroscopy

All NMR experiments were carried out on a DSX 400 Instrument (Bruker Analytik GmbH, Germany) with a 9.4 Tesla wide-bore magnet. Solid state ^{13}C NMR spectra were acquired with a CP-MAS probe for 4 mm rotors at 100.6 MHz. H_1 field strength for CP and proton decoupling was 89.3 kHz corresponding to $2.8 \mu\text{s}$ 90° pulse length. For proton decoupling, TPPM⁸ pulse sequence was employed. Contact time of 1.5 ms, pulse repetition delay of 2 s, spectral width of 16 kHz were used. Sample spinning rate was 2.5 kHz and stability of spinning was within ± 4 Hz. For synchronized MAS 2D experiments, the pulse sequence described in Figure 2 was used and 64 data files were acquired with delay time t_1 incremented by $2.5 \mu\text{s}$ from $2.5 \mu\text{s}$ to $160 \mu\text{s}$. Number of scans for each t_2 data file was 20 for oriented sample and 10 for powdered sample. Line broadening of 10 Hz was applied for F_2 dimension process. For ^{13}C MAS spectra without CP, pulse sequence delay time of 750 s, pulse length of $1.9 \mu\text{s}$, spinning rate of 10kHz were used³; H_1 field strength for proton

decoupling and carbon 90° pulse was 65.8 kHz. Number of acquisition of each MAS spectrum without CP was 46 ~ 64.

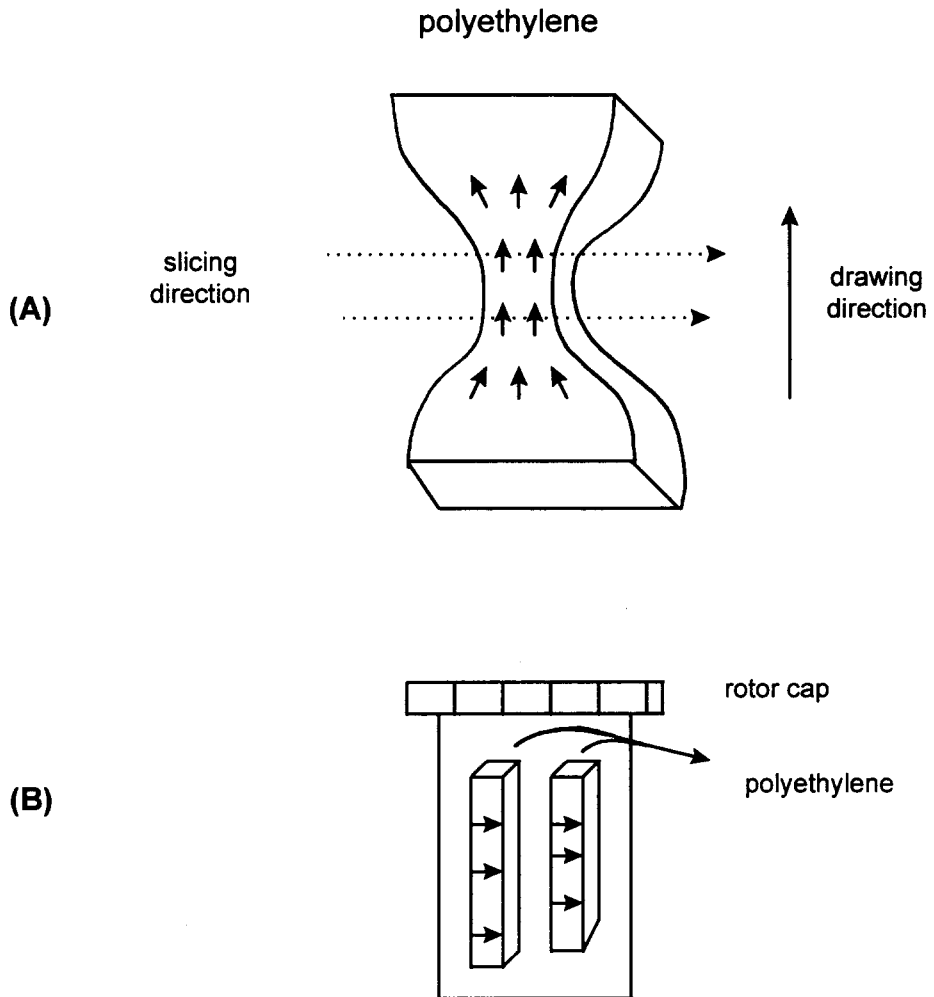


Fig. 1. Preparation of drawn PE. (A) PE was drawn along the direction of the arrow and sliced 90° to drawing direction. (B) The sliced PE was put into a rotor and the drawing direction was 90° to the rotor axis.

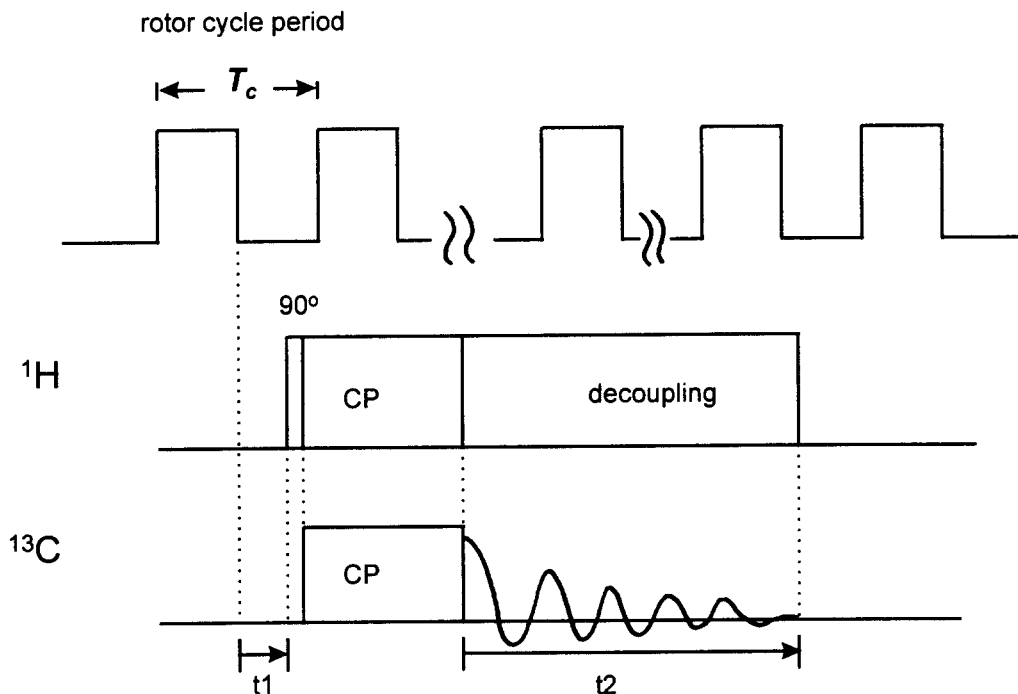


Fig. 2. Pulse sequence for a synchronized MAS 2D experiment. Starting point of the pulse sequence for each file in F_2 dimension has a constant delay time, t_1 , versus a rotor cycle. Delay time, t_1 , was incremented by $2.5 \mu\text{s}$.

RESULTS AND DISCUSSION

From solid state ^{13}C MAS NMR spectra of PE, in spite of the fact that typically methylene peaks only are observed, information on crystalline phases existing in the sample can be obtained.³ Methylene carbons from different phases appear at different chemical shifts; at 34.2 ± 0.3 , 32.8 ± 0.3 , and 31.3 ± 0.3 ppm, from monoclinic, orthorhombic, and amorphous phases, respectively.³ Original PE before drawing or powdering had only methylene peaks from orthorhombic crystalline and amorphous phases in the ^{13}C MAS NMR spectra.³ We observed a new methylene peak at 34.2 ± 0.3 ppm after the PE was powdering at 77 K, which was interpreted as indicating solid-solid phase transition from orthorhombic to monoclinic crystalline phase.³ Our drawn PE also showed three methylene peaks from monoclinic, orthorhombic, and amorphous phases in its ^{13}C CP-MAS spectra (Fig. 3A) indicating that solid-solid phase transition induced from orthorhombic to monoclinic crystalline phase during drawing process. From peak area integration of ^{13}C MAS NMR

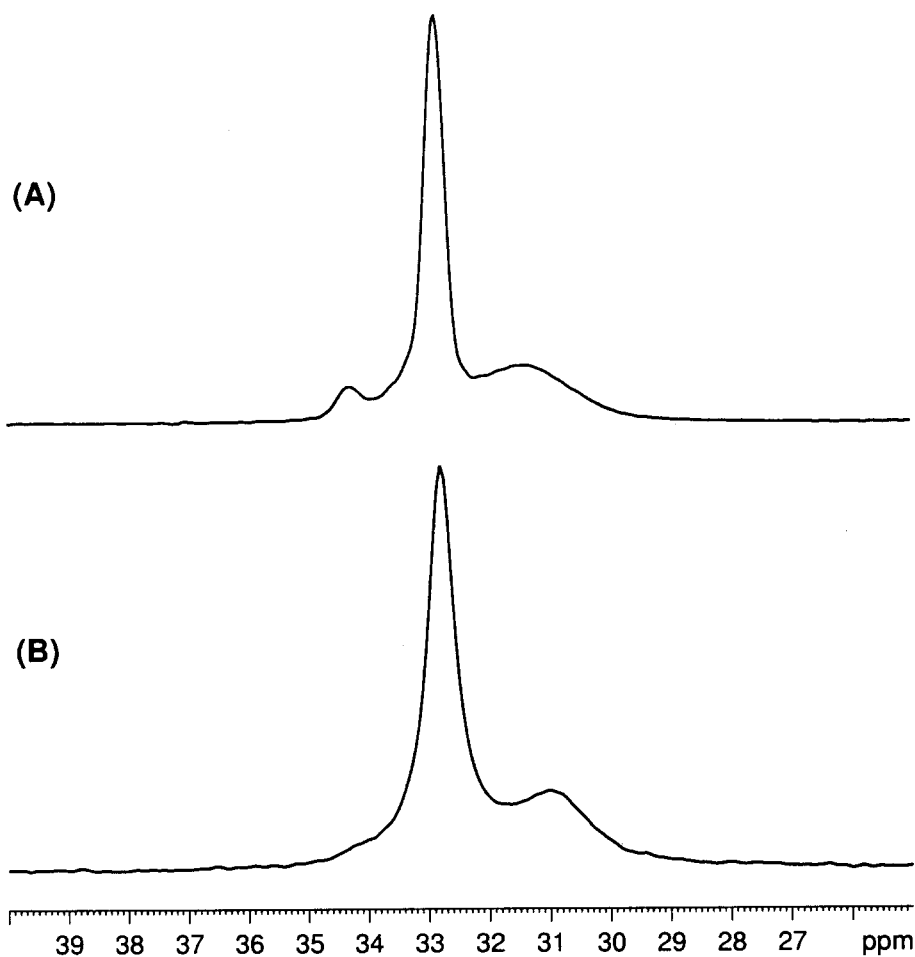


Fig. 3. ^{13}C CP-MAS spectrum of (A) drawn PE and (B) PE before drawing. Number of acquisition for (A) and (B) are 20 and 80, respectively.

Table 1. Relative Areas of Methylene Peaks from Different Phases.*

Sample	monoclinic phase	orthorhombic phase	amorphous
original PE	0 %	50 %	50 %
drawn PE	6 %	43 %	51 %
powdered PE	18 %	35 %	47%

*Error range in the measurement is $\pm 3\%$.

spectra obtained without CP (not shown here due to poor signal to noise ratio), population of each phase was calculated and summarized in Table 1.

Orientations of crystalline phase domains in our PE before drawing were found to be random.³ Molecular ordering induced by drawing was checked with a sync-MAS 2D technique. In Fig. 4, the spectra of drawn PE are stacked- plotted. For more spinning side bands, slow spinning rate of 2.5 kHz and high magnetic field of 9.4T were used. At least two spinning side bands at each side of the center peaks are shown.

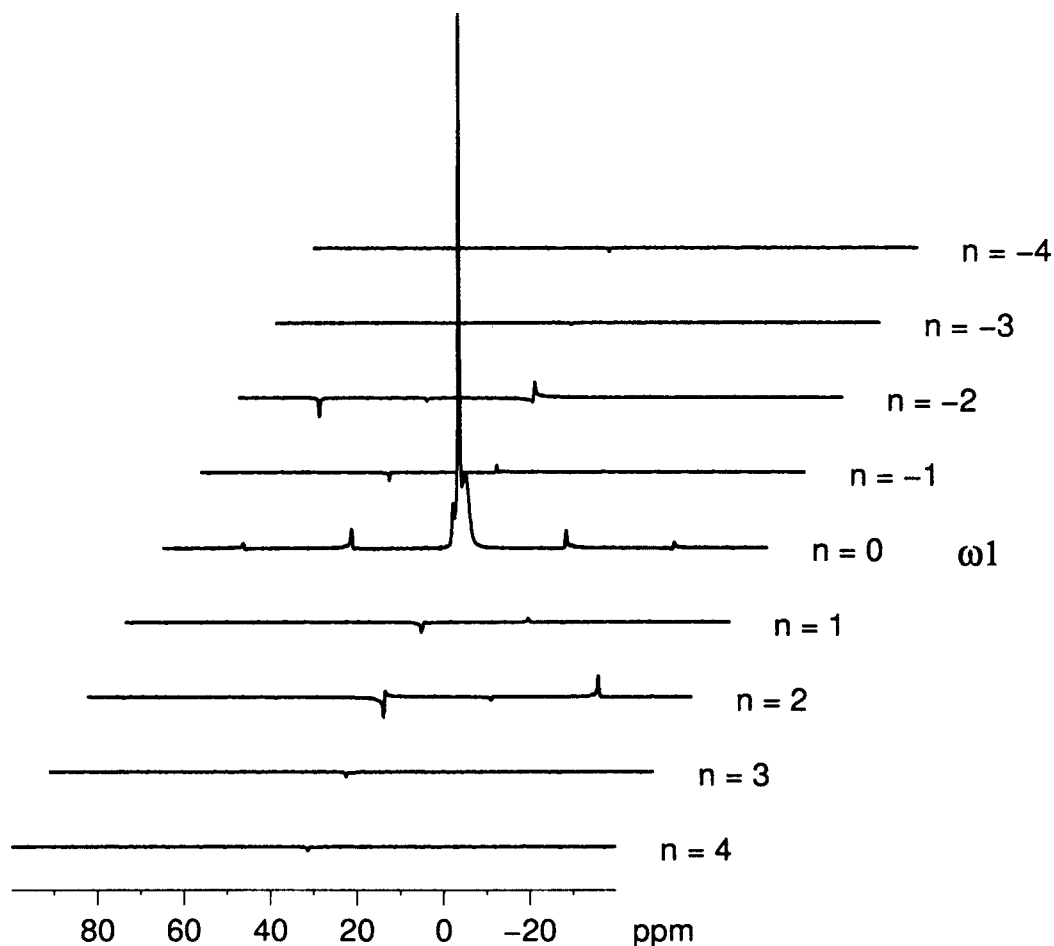


Fig. 4. Stacked plot of 2 dimensional synchronized MAS spectra of drawn PE.

In the spectrum along ω_1 at the center (denoted as $n = 0$), we see a 1 dimensional ^{13}C CP-MAS spectrum of PE in which there are three methylene center peaks at the center and two small spinning side bands at each side of the center peaks 2.5 kHz apart. Spinning side bands relatively large intensities are observed in the spectra along ω_2 for fixed ω_1 values denoted by $n = 2$ and -2 . The methylene center peaks also show greater intensities in the spectra along ω_2 for ω_1 at $n = 2$ and -2 than those in the spectra along ω_2 for ω_1 at $n = 1$ and -1 . In contrast, sync-MAS 2D spectra of powdered PE (Fig. 5) have peak intensities mostly in the spectrum along ω_2 for ω_1 at $n = 0$.

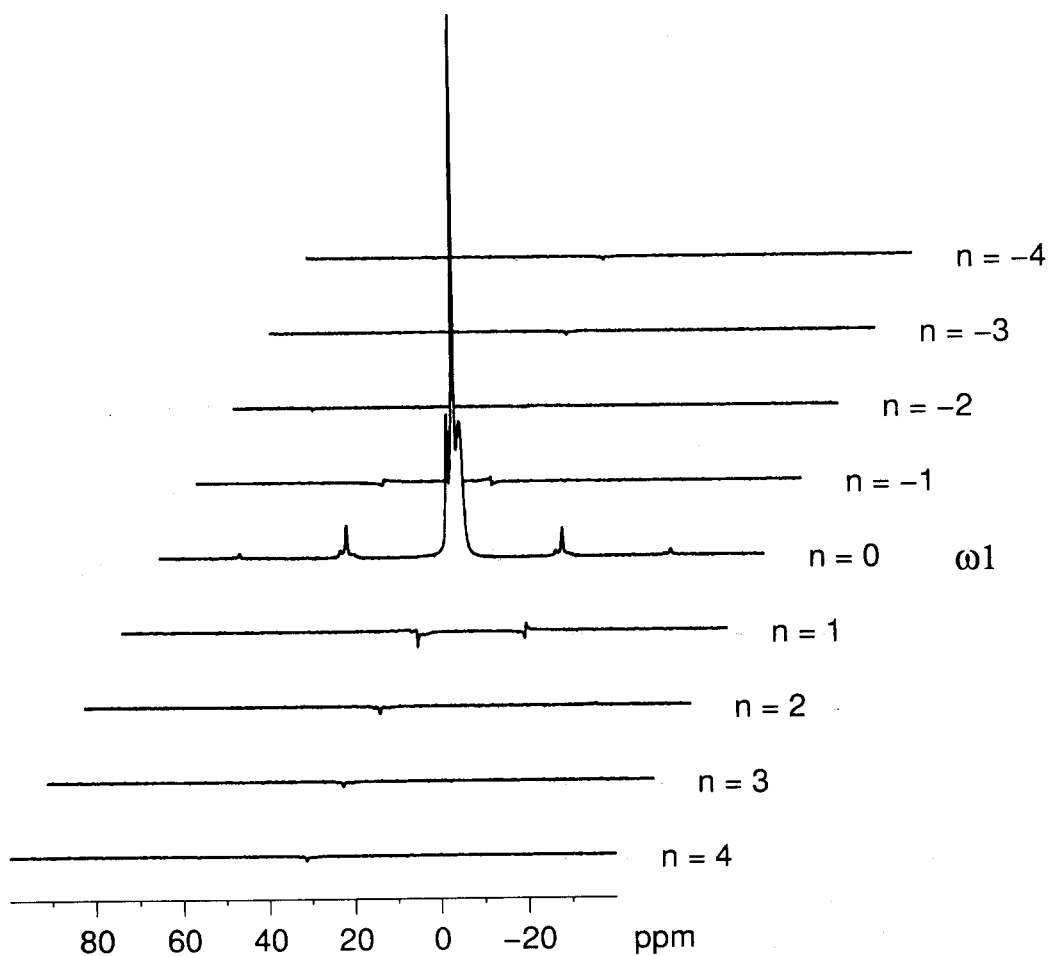


Fig. 5. Stacked plot of 2 dimensional synchronized MAS spectra of powdered PE.

The intensities of peaks drastically and monotonically decreases as the spectrum along ω_2 for a specific ω_1 value moves away from the center ($n = 0$); it can be regarded that only the spectrum along ω_2 for ω_1 at $n = 0$ has discernible intensities within experimental error. The sync-MAS 2D spectra of powdered PE are typical for samples with random orientation or ordering axis parallel to a rotor axis. If samples have molecular ordering axis not parallel to a rotor axis, sync-MAS 2D spectra would manifest distribution of intensities among spectra along ω_2 for various ω_1 values. Comparison of our sync-MAS 2D spectra of powdered PE and drawn PE clearly indicates that drawing induced molecular ordering of PE. If this ordering axis is vertical to the drawing axis, the sync-MAS 2D spectra would be similar to those of powdered PE. It is known that polymer molecules are aligned along drawing direction in general. Thus, we may expect alkyl chains are aligned along the drawing direction; the drawn PE pieces were aligned in a rotor such that the drawing direction be vertical to a rotor axis. For calculation of ordering axis and degree of order, spectrum simulation is necessary which is currently in progress. By simulation of the spectra with intensity distribution, ordering of specific molecular segments or carbon sites can be obtained.^{4,5}

In summary, we report here that drawing not only increased molecular ordering in PE but also induced solid-solid phase transition from orthorhombic to monoclinic crystalline phase. For this, methylene peak area integration in ^{13}C MAS NMR spectra and a sync-MAS 2D technique with ^{13}C CP were used.

Acknowledgments

The author would like to thank Dr. Stefan Steuernagel at the Bruker Analytik GmbH (Germany) for technical support in NMR experiments. Professor Hans W. Spiess and Dr. Daniel Maring at the Max-Planck-Institute for Polymer Science (Germany) are also acknowledged for helpful discussion on the synchronized MAS techniques. Dr. Jae Kap Jung at the Korea Basic Science Institute and Dr. Sungok Han at the Korea Institute of Energy Research are thanked for deconvolution of spectra and generous supply of original PE sample, respectively. This work was supported by grants (for 1997 and 1998) from the Ministry of Science and Technology (MOST), the Republic of Korea.

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